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A new thin-film electroluminescent material— $\text{ZnF}_2:\text{Mn}^{2+}$

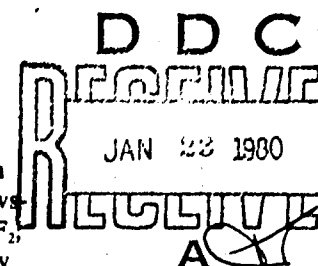
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Both ac and dc orange (580 nm) electroluminescence (EL) are reported for thin films of $\text{ZnF}_2:\text{Mn}$ sandwiched between SiO semi-insulating films. All layers are formed by vacuum evaporation and no postdeposition annealing is required. Unique power input and efficiency-vs-frequency characteristics are observed, in part due to the 0.1-s lifetime of excited Mn in ZnF_2 ; hysteresis in the brightness-voltage characteristic occurs. The brightness and power efficiency are found to be, respectively, 10 fL and 0.5% under suitable operating conditions.

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High-field collision-excitation electroluminescence (EL) has become a current area of active research as a result of the application of thin-film technology to form relatively stable EL devices with power efficiencies approaching 1% and with hysteresis in the brightness-voltage characteristic permitting information storage as well as display.¹ The major research has involved evaporated $\text{ZnS}:\text{Mn}$ sandwiched between sputtered or electron-beam evaporated Y_2O_3 ¹⁻³; similar devices have been made with $\text{ZnSe}:\text{Mn}^{2+}$; related work has been reported on crystals of $\text{CdF}_2:\text{Mn}$ in MIS structures⁴; EL has been studied with rare earth dopants in place of Mn in these materials⁵—in all the aforementioned, a high temperature postgrowth anneal is required.

$\text{ZnF}_2:\text{Mn}$ is unique among luminescent materials in being capable of rather efficient cathodoluminescence in the form of transparent thin films formed by vacuum evaporation.⁷ No postdeposition anneal is needed. Its lower refractive index minimizes the internal trapping of the emission which reduces substantially the efficiency of ZnS thin films. The ZnF_2 and $\text{ZnF}_2:\text{Mn}$ have the rutile structure and are weakly *N*-type semiconductors with low electron mobility;⁸

thus, these materials differ markedly in structure and electronic properties from CdF_2 and $\text{CdF}_2:\text{Mn}$.

The layered thin films were deposited in sequence on conducting Corning glass 7059 (SnO_2 coated to 100 Ω /square resistance) maintaining the vacuum at less than 2×10^{-5} Torr. Both the $\text{ZnF}_2:\text{Mn}$ and SiO were outgassed before evaporation. The $\text{ZnF}_2:\text{Mn}$ used in the evaporation had been mixed by weight from ZnF_2 and MnF_2 , sintered at 800 °C and ground to a powder. Compositions investigated were 0.5–5-mol% MnF_2 . The substrate was slightly above room temperature. Typical sequential deposits were 5000 Å of SiO , 2000 Å of $\text{ZnF}_2:\text{Mn}$, and 5000 Å of SiO . Selected edges were masked in order to make electrical contacts. Finally, the second electrode of aluminum was deposited by evaporation through a mask.

The SiO is only semi-insulating, so that dc EL, as well as ac EL, is observed. The highest efficiencies are measured at low frequencies, e.g., 10 cps. The current *I* in the external

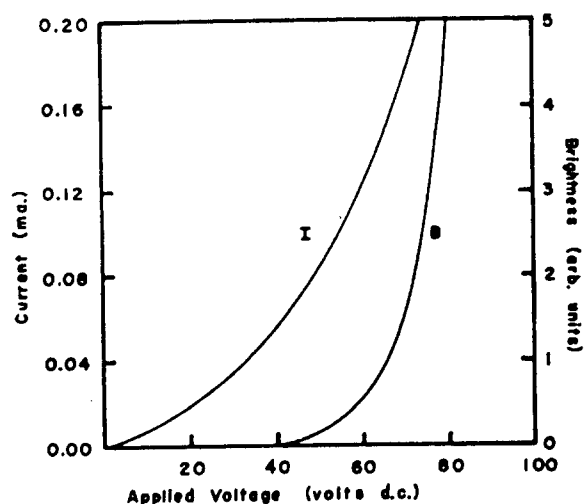


FIG. 1. Current *I* and brightness *B* versus applied dc voltage *V* for $\text{ZnF}_2:0.011\text{Mn}$ with the typical SiO and fluoride thicknesses.

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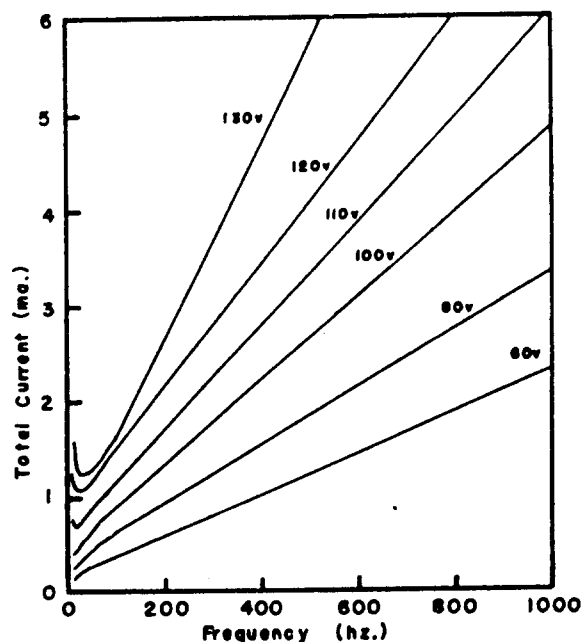


FIG. 2. Total current *I* versus frequency *f* for different applied ac voltages V_{rms} . 90% of the data points fall within ± 20 cps and ± 0.1 ma for the curve at highest *V* and within ± 10 cps and ± 0.02 ma for the curve with lowest *V*.

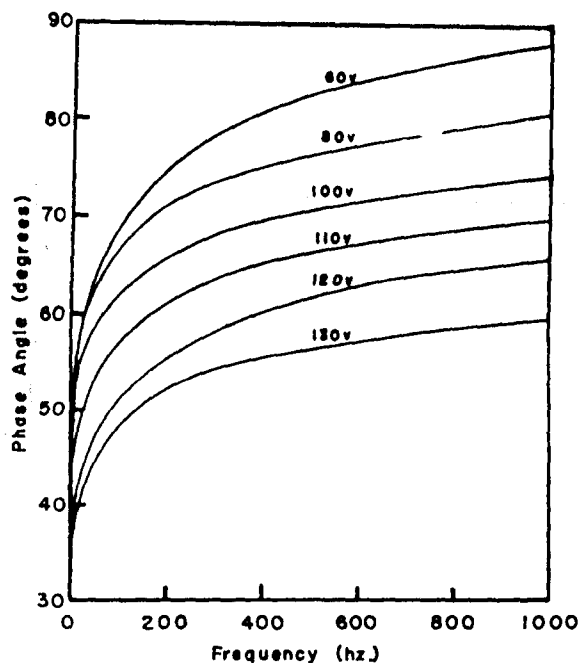


FIG. 3. Phase angle ϕ versus frequency f for different V_{rms} . 90% of the data points fall within ± 20 cps and $\pm 3^\circ$ of the fitted curves.

circuit is shown in Fig. 1 for dc, and as a function of frequency for applied ac voltages V in Fig. 2. The brightness, B versus V is also shown on Fig. 1. In order to obtain the input power P for ac the phase difference ϕ between I and V was measured on a dual trace Tektronix 545 scope and is plotted versus f in Fig. 3 for different V . The device responds electrically like a non-Ohmic resistor in parallel with a capacitor so that with increasing f the current generally becomes more capacitive, but at higher V the current remains more resistive to higher f . The non-Ohmic character is evident from the dc measurements. Thus, from the data in Figs. 2 and 3, the P can be obtained: $P = IV \cos \phi$. Except for some structure at low f , P is approximately linear with f , with greater slope at higher V .

The brightness B was measured as a function of V and f . Hysteresis in $B(V)$ was observed and is shown in Fig. 4. This characteristic is similar to those reported for $ZnS : Mn^{1,2}$ and for $ZnSe : Mn$.⁴ The electrical characteristics described in the preceding paragraph are for the decreasing voltage $B(V)$ curve. The emission spectrum of the $ZnF_2 : Mn$ with EL excitation is the same as previously reported for photo- and cathode-ray excitation, peaking at 580 nm.⁹

Absolute brightnesses were measured by two independent methods: comparison with a standard lamp illuminating a diffusing screen, and a calibrated Tektronix J16 digital photometer. Brightnesses of 10 fL were attained with reasonable stability; higher values resulted in deterioration of present devices. Combined with power input data, power efficiencies η of 0.5% were obtained at low frequencies, e.g., 10–30 cps. At higher f , η decreases approximately as $1/f$.

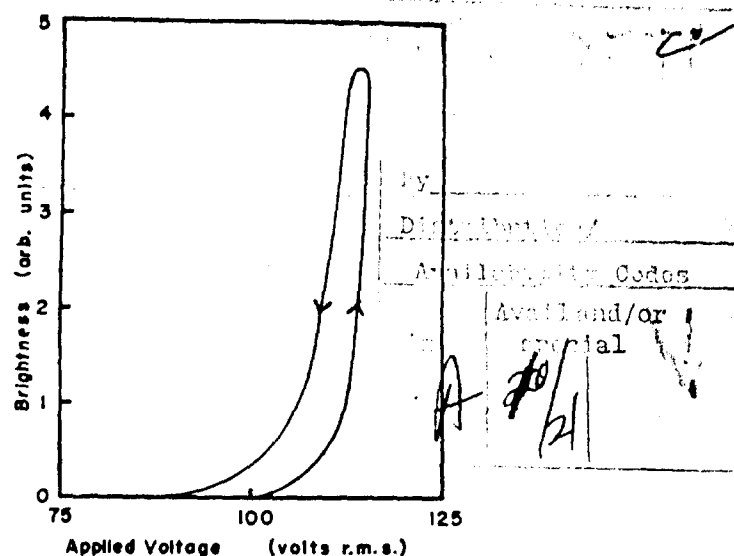


FIG. 4. Brightness-voltage hysteresis curve at 500 cps for $ZnF_2 : 0.016 Mn$.

The $\eta \propto 1/f$ and $P \propto f$ at the higher f mean, of course, constant B at constant V , independent of f , suggesting saturation. From the radiative lifetime of 0.1 sec for Mn in $ZnF_2 : Mn$ and for concentrations of 1-mol% Mn, saturation of a 2000-Å-thick layer is predicted at 10 mW of radiation/cm². We observe as much as 0.1 mW/cm² of radiation which means that 1% of the Mn are homogeneously excited simultaneously or that 1% of the volume is excited to saturation. This estimate neglects internal trapping and absorption in the SiO. No inhomogeneities were observed microscopically under normal conditions of excitation.

Summarizing, layered thin-film $ZnF_2 : Mn$ device electroluminescence at low frequencies with efficiencies approximately equal to those of other high field EL devices and with hysteresis in the $B(V)$ characteristic have been observed. We are investigating $ZnF_2 : Mn$ devices with better insulating layers to attain higher efficiency and stability. The absence of a postdeposition anneal allows for the possibility of deposition on low melting substrates such as plastics.

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